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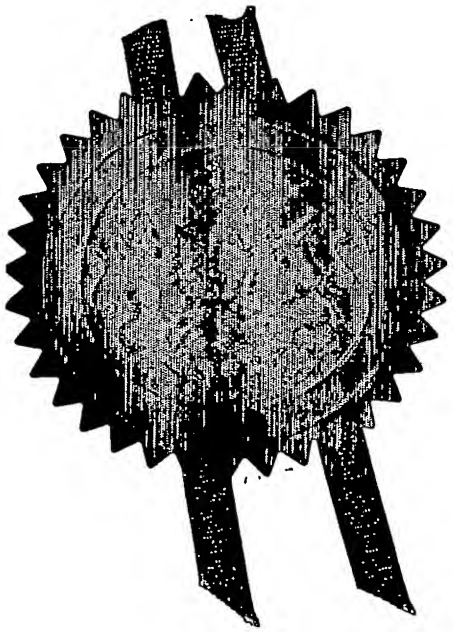

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Dated 7 November 2003

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23DEC02 E772794-1 D02825
P01/7700 0.00-0229770.3

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1. Your reference — 302525/CMH/JE

2. Patent application number *(The Patent Office will fill in this part)* — 20 DEC 2002 — 0229770.3

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   SASOL TECHNOLOGY (UK) LTD
   Purdie Building
   North Haugh
   St Andrews, KY16 9ST
   SCOTLAND, U.K.

   08531808001
   Patents ADP number *(if you know it)*

   If the applicant is a corporate body, give the country/state of its incorporation — British

4. Title of the invention — Olefinic Metathesis in the Presence of Phenolic Compounds

5. Name of your agent *(if you have one)*

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

   PAGE WHITE & FARRER
   54 Doughty Street,
   London WC1N 2LS,
   United Kingdom

   Patents ADP number *(if you know it)* — 1255003

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

   a) any applicant named in part 3 is not an inventor, or
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Patents Form 1/77

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11. I/We request the grant of a patent on the basis of this application.

Signature White & Co Date 20.12.2002

Page White and Farrer

12. Name and daytime telephone number of person to contact in the United Kingdom: Jane Evenson (020) 7831-7929

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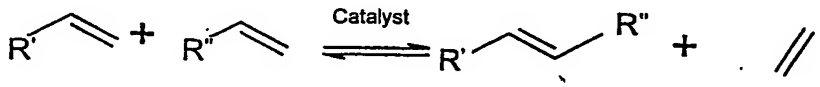
FIELD OF THE INVENTION

This invention relates to enhancement of a metathesis reaction between at least two non-cyclic olefins which are the same or different.

BACKGROUND ART

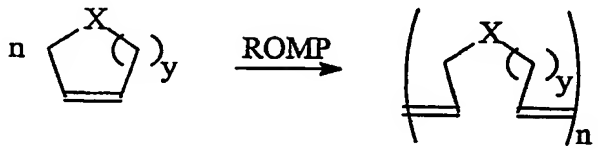
There is considerable interest regarding the formation of carbon-carbon bonds *via* olefin metathesis. The quest for highly active olefin metathesis catalysts has prompted considerable research efforts to develop olefin metathesis systems capable of tolerating a variety of functional groups. Ruthenium-based catalysts in particular have proven to be useful in catalysing olefin metathesis reactions, including cross metathesis, ring-closing metathesis (RCM) and ring-opening metathesis polymerisation (ROMP) reactions.

Olefin metathesis refers to the metal-catalysed redistribution of carbon-carbon double bonds. CM can be described as a metathesis reaction between two non-cyclic olefins, which may be the same or different, for example:

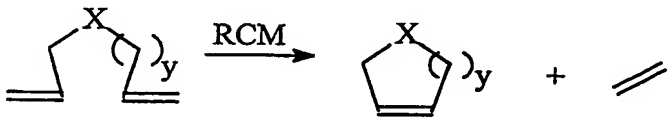


Where the olefins are the same, the reaction is known as self metathesis.

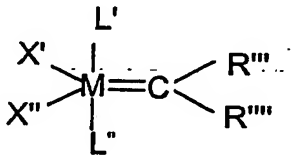
ROMP is a variant of olefin metathesis reactions wherein cyclic olefins produce polymers and co-polymers, for example:



RCM represents a process in which an acyclic diene is cyclised to produce a cycloalkene, for example;



As indicated above metathesis reactions take place in the presence of a catalyst. Grubbs-type catalysts are ruthenium alkylidene complexes of the type shown below, and are highly active single component pre-catalysts for alkene metathesis reactions.



wherein:

M is ruthenium

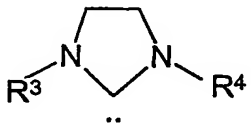
X^{I} and X^{II} are independently an anionic ligand such as a halide;

R^{III} and R^{IIII} are independently hydrogen or an organyl group; and

L^{I} and L^{II} are independently a neutral electron donor ligand.

If each of L^I and L^{II} comprises a compound containing phosphorus wherein phosphorus is co-ordinated to M, then the catalyst is known as a Grubbs first generation catalyst, hereinafter referred to as Grubbs 1.

If one of L^I and L^{II} is not as defined for Grubbs 1, and especially if at least one of L^I or L^{II} comprises an N-heterocyclic carbene compound wherein the carbene carbon atom is co-ordinated to M, then the catalyst is known as a Grubbs second generation catalyst, hereinafter referred to as Grubbs 2. Such a carbon containing compound may for example comprise a substituted imidazolium ligand such as:



With regards to the production of bulk chemicals one of the limitations is the need to use relatively high levels of ruthenium compounds. This is often in excess of 1 mol% of substrate. This destroys the economic viability of such processes. The use of suitably low catalyst concentrations is also confounded by the presence of impurities in typical alkene feedstocks derived from primary processes such as naphtha cracking or the Fischer-Tropsch conversion of synthesis gas. During a study to identify possible catalyst poisons present in such feed streams it was surprisingly found that the addition of relatively low concentrations of phenol has a beneficial effect on catalyst performance in cross-metathesis, instead of the poisoning or retarding effect which was expected. In addition, the addition of

phenol was surprisingly found to impart to the catalyst a greater tolerance to feed impurities and known catalyst poisons. These poisons are described in detail, later in this specification.

Thus in the presence of phenol it was found that CM reactions could be carried out at low ruthenium concentrations, giving good conversions of feedstock, high selectivity to desired products, and greater tolerance to feed impurities.

Such an effect has not been reported for this reaction before. In Macromolecules 2000, 33, 717-724 and in the Journal of Molecular Catalysis A. 2000, 160, 13-21, it was reported that the nature of the polymer formed by the ROMP reaction of two cyclic monomers was altered by running the reaction in chlorophenol as a solvent. This change was attributed to an unquantified increase in catalyst activity. The authors suggested that this was due to the phenolic solvent increasing the electrophilicity of the ruthenium centre.

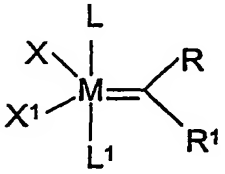
However the report of Grubbs and co-workers (J.Am.Chem.Soc. 1993, 115,9858-59) commented that whilst making the metal centre more electrophilic does lead to changes in the relative propagation rate of the ruthenium carbene centre in the polymerisation of norbornene such complexes do not show improved activity for cross metathesis of pent-2-ene. This again suggests that the above effect is restricted to propagation rates of certain ROMP reactions and is not generally applicable to all types of metathesis reactions.

The effect reported for the present invention is significant at much lower levels of phenol addition, typically 0.02 mol l^{-1} versus the bulk solvent employed in the above publication. Indeed examples shown below clearly indicate that there is no benefit to be gained by increasing the phenol concentration in this reaction.

The effect is not general for all metathesis reactions, again it is shown in the examples that phenol actually suppresses the rate of RCM. Neither is the effect uniform for all phenols and related compounds. Neither is it uniform for all metathesis catalysts, indeed the performance of the Grubbs 2 catalyst is diminished by the addition of phenol.

DISCLOSURE OF THE INVENTION

According to the present invention there is provided a metathesis reaction between at least two olefinic compounds which are the same or different, each olefinic compound comprising a non-cyclic olefin or a compound which includes a non-cyclic olefinic moiety; the metathesis reaction being carried out in the presence of a catalyst of the formula:



..... (I)

wherein:

M is Ruthenium or Osmium;

X and X^1 are independently selected from an anionic ligand;

R and R^1 are independently selected from H or an organyl group; and

L and L^1 are independently selected from any neutral electron donor ligand.

and the metathesis reaction being characterised therein is carried out in the presence of a phenolic compound in the form of a phenol or a substituted phenol.

According to another aspect of the present invention there is provided the use of a phenolic compound in the form of a phenol or a substituted phenol in a metathesis reaction between at least two olefinic compounds which are the same or different, each olefinic compound comprising a non-cyclic olefin or a compound which includes a non-cyclic olefinic moiety, and the metathesis reaction being carried out in the presence of a catalyst of formula (I) as defined above.

The metathesis reaction may be enhanced by the phenolic compound and it may be enhanced in at least one of the following ways:

i) increased lifetime of the catalyst;

ii) increased resistance of the catalyst to olefin feed poisons, including oxygen-containing compounds;

iii) increased selectivity of the metathesis reaction in respect of at least one of the following aspects:

a. reduced isomerisation of the starting olefinic compound(s);

b. reduced formation of secondary metathesis products; and

iv) increase in the conversion of the starting olefinic compound(s);

It has been found (from the examples below) that the less expensive Grubbs 1 catalysts with a phenolic compound provide results comparable to that obtained with the more expensive Grubbs 2 catalyst.

Preferably the metathesis reaction produces one or more non-cyclic olefins or one or more compounds which include a non-cyclic olefinic moiety.

The starting olefinic compound(s)

Preferably the metathesis reaction is between at least two non-cyclic olefins which are the same or different. Preferably at least one, but preferably all of the at least two non-cyclic olefins comprise an olefin with a single double bond. Preferably at least one, but preferably all of the at least two non-cyclic olefins comprise a 1-alkene. The 1-alkene may comprise a non-branched linear alkene for example 1-octene or 1-heptene.

In one embodiment of the invention the metathesis reaction may be between at least two different non-cyclic olefins, preferably between only two different non-cyclic olefins. In a further embodiment of the invention the one non-cyclic olefin may comprise ethylene and the second non-cyclic olefin may comprise an internal olefin.

In an alternative embodiment the metathesis reaction may be between two non-cyclic olefins which are the same. The non-cyclic olefin may be an olefin with a single double bond, preferably a 1-alkene, preferably a non-branched linear 1-alkene (for example 1-octene or 1-heptene).

In an alternative embodiment the metathesis reaction may be between at least two non-cyclic olefins of which at least one is derived from a Fischer-Tropsch reaction. Such a feedstream is often very complex and may contain linear and branched 1-alkenes, linear and branched internal alkenes, as well as alkanes, aromatics and various oxygenated impurities.

The non-cyclic olefinic feedstocks may further contain impurities selected from the group consisting of carbonyls, alcohols, aromatic components, dienes, trienes and aldehydes. These impurities are known to act as poisons which interfere with the catalytic activity of the catalysts of this invention, in the absence of a phenolic compound. The interference with the catalyst may be in the form of retardation of the conversion of the starting olefin, or by permanently deactivating

the catalyst. Specific examples of such poisons, which examples are not an exhaustive list, are acetone, ethanol, toluene, cycloheptatriene, cyclooctadiene, 1-hexanol, 2-hexanone, hexanal, 3-hexyne.

The catalyst

With reference to formula (I) M is preferably Ru.

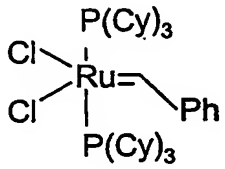
X and X^1 may be independently selected from hydrogen; halide; or a compound selected from the group consisting of C_1 – C_{20} alkyl; aryl; C_1 – C_{20} alkoxide; aryloxide; C_3 – C_{20} alkyldiketonate; aryldiketonate; C_1 – C_{20} carboxylate; arylsulfonate; C_1 – C_{20} alkylsulfonate; C_1 – C_{20} alkylthiol; aryl thiol; C_1 – C_{20} alkylsulfonyl; and C_1 – C_{20} alkylsulfinyl, the compound being optionally substituted with one or more other moieties selected from the group consisting of C_1 – C_{10} alkyl; C_1 – C_{10} alkoxy; aryl and halide. Preferably X and X^1 are each independently selected from the group consisting of halide; CF_3CO_2; CH_3CO_2; CFH_2CO_2; $(CH_3)_3CO$; $(CF_3)_2(CH_3)CO$; $(CF_3)(CH_3)_2CO$; PhO; MeO; EtO; tosylate; mesylate; and trifluoromethanesulfonate. Preferably X and X^1 are each independently selected from halide. Preferably X and X^1 are each chloride.

R and R^1 are each independently selected from hydrogen or an organyl selected from the group consisting of C_1-C_{20} alkyl; C_2-C_{20} alkenyl; C_2–C_{20} alkynyl; aryl; C_1–C_{20} carboxylate; C_1-C_{20} alkoxy; C_2-C_{20} alkenyloxy; C_2–C_{20} alkynyloxy; aryloxy; C_2-

C_{20} alkoxycarbonyl; C_1-C_{20} alkylthiol; aryl thiol; C_1–C_{20} alkylsulfonyl and C_1-C_{20} alkylsulfinyl, the organyl being optionally substituted with one or more moieties selected from the group consisting of C_1–C_{10} alkyl; C_1–C_{10} alkoxy; aryl; and a functional group selected from the group consisting of hydroxyl; thiol; thioether; ketone; aldehyde; ester; ether; amine; imine; amide; nitro; carboxylic acid; disulfide; carbonate; isocyanate; carbodiimide; carboalkoxy; carbamate; and halogen. Preferably R is hydrogen and R^1 is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C_1-C_5 alkyl; C_1–C_5 alkoxy; phenyl; and a functional group selected from the group consisting of hydroxyl; thiol; thioether; ketone; aldehyde; ester; ether; amine; imine; amide; nitro; carboxylic acid; disulfide; carbonate; isocyanate; carbodiimide; carboalkoxy; carbamate; and halogen. Preferably R is H and R^1 is phenyl or – $C{=}C(CH_3)_2$.

L and L^1 are each independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, amine, amide, imine, nitrosyl and pyridine. Preferably L and L^1 are independently a phosphine preferably a phosphine of the formula $PR^3R^4R^5$, wherein R^3, R^4 and R^5 are each independently aryl, C_1 – C_{10} alkyl or cycloalkyl. Preferably L and L^1 are each independently selected from the group consisting of –P(cyclohexyl)$_3$; -P(cyclopentyl)$_3$; -P(isopropyl)$_3$; and –P(phenyl)$_3$. Preferably L and L^1 may be a phosphacycloalkane or phosphabicycloalkane such as eicosyl phoban. Preferably L and L^1 are the same.

In one embodiment of the invention the catalyst of formula I may comprise:



..... (II)

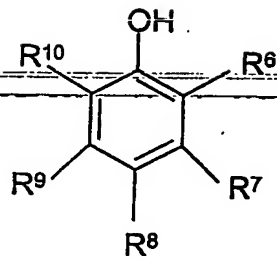
wherein Cy is cyclohexyl.

In one embodiment of the invention the catalyst may be prepared prior to addition of the catalyst to the metathesis reaction. In an alternative embodiment of the invention the catalyst may be prepared in situ in the reaction medium of the metathesis reaction.

The phenolic compound

In one embodiment of the invention the phenolic compound may comprise a phenol, including phenol.

In another embodiment of the invention the phenolic compound may comprise a substituted phenol, wherein one or more of the hydrogen atoms on the arene ring of the phenol is substituted. The substituted phenol may comprise a substituted phenol of the formula:



wherein R^6 R^7 R^8 R^9 and R^{10} are each independently selected from H and any suitable functional group, and at least one of R^6 R^7 R^8 R^9 and R^{10} is not, H. The functional group may comprise (but is not limited to) halide; oxy organyl (including alkoxy), benzoate, carboxylate, alkyl (for example Me, Et, ^{t}Bu), phenol, alkylthio, aryl, alkylsulfonate, tosylate, mesylate, cycloalkyl, arylsulfonate, alkylketone, alkyldiketone, alkylsulfinyl, phosphine, phosphinate, phosphate, hydroxyl, alkoxycarbonyl, amino, nitro, haloalkyl, nitrile.

In another embodiment of the invention the phenolic compound may comprise an optionally substituted polyaromatic phenol e.g. napthol.

The substituted phenol may be selected from the group consisting of cresol; Et-phenol (including 4-Et-phenol); OMe – phenol (including 4-OMe-phenol); CN-phenol (including 4-CN-phenol); chlorophenol (including 4-chlorophenol) fluorophenol (including 4-fluorophenol), iodophenol (including 4-iodophenol) CF_3-phenol (including 4-CF_3-phenol; 2,6-di-tert-butyl-4-methylphenol (BHT); 1-naphtol; 2-naphtol; hydroquinone; and catechol.

The concentration of the phenolic compound may be varied as required. In one embodiment of the invention the molar ratio of catalyst to phenolic compound may be from 1 to 5000 molar equivalents of phenolic compound to ruthenium, preferably in the range of 200 to 1000 molar equivalents.

The present invention also relates to an olefin produced by the process or use set out above.

The invention will now be further described by means of the following non-limiting examples.

Examples

Unless otherwise stated, the general experimental procedure for the metathesis reactions of the examples were performed in a 250 mL round-bottom flask. 1-Octene was purified by passing it through an alumina column and it was stored over alumina in the absence of light. The stock 1-octene solution was degassed with N_2 30 minutes before use, and 20 mL was transferred to a 250 mL flask containing the phenol additive. [Unless stated otherwise the control contained no phenol additive]. The solution was degassed at room temperature for 30 minutes before being heated to 50 °C. A Grubbs 1st generation catalyst of formula II (referred to as G1) was weighed into a custom-made miniature aluminium weighing tray. An amount of 11.2 mg of the catalyst provided a Ru concentration

of 100ppm. The weighing tray containing the catalyst was added, and the reaction stirred for 6 hours. Samples were taken thereafter every 10, 30, 60, 120, 180, 240 and 360 minutes and analysed by GC-FID. Conversions are reported as the molar% 1-octene which was converted to the desired 7-tetradecene product.

Unless stated otherwise the reference to equivalents of a compound refers to molar equivalents of the compound to the catalyst. For example 500eq of phenol refers to a phenol to catalyst molar ratio of 500:1.

Example 1 - The phenol enhancement effect.

An increased conversion of 1-octene to the desired 7-tetradecene product was observed for the metathesis of 1-octene when 500 equivalents of phenol was added to the reaction mixture (Table 1). Under these conditions, no detectable (by GC) amounts of isomerised octene or secondary metathesis products (SMP's) were observed. Furthermore, the catalyst was active even after four hours, in marked contrast to the control experiment where no phenol was added. In an effort to verify the results obtained above, the reaction was repeated. These results indicate that the reaction can be readily reproduced.

Table 1: Metathesis of 1-octene with G1 (no phenol) vs G1 + phenol (500 eq) at 50°C.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 500 eq phenol	82.0 %
G1 + 500 eq phenol (repeated)	86.6 %

Example 2 - Effect of phenol concentration

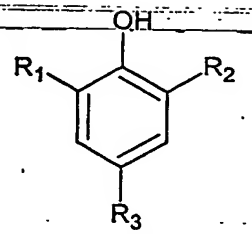
The 1-octene metathesis reactions were performed using 200, 500 and 1000 equivalents of phenol, respectively, and the results are shown in Table 2. Under these conditions, optimum performance is achievable with either 500 or 1000 equivalents of phenol.

Table 2: Metathesis of 1-octene with G1 + phenol (200, 500 and 1000eq).

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 200 eq phenol	63.2 %
G1 + 500 eq phenol	82.0 %
G1 + 1000 eq phenol	77.4 %

Example 3 - Effect of substitution on phenol

In an effort to asses the effect of substitution on the benzene ring of the phenol on the formation of tetradecene in 1-octene metathesis, 500 equivalents of compounds 1-6 were added to the reaction mixture and the results are summarized in Table 3.



(1) R_3=OMe; R_1= R_2=H
(2) R_3=Me; R_1= R_2=H
(3) R_3=Cl; R_1= R_2=H
(4) R_3=CF_3; R_1= R_2=H
(5) R_3=I; R_1= R_2=H
(6) R_3=F; R_1= R_2=H

Table 3: Metathesis of 1-octene with substituted phenols

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 500 eq 4-Cl-phenol	58.2 %
G1 + 500 eq 4-CF_3-phenol	64.8 %
G1 + 500 eq 4-I-phenol	71.0 %
G1 + 500 eq 4-OMe-phenol	71.8 %
G1 + 500 eq phenol	82.0 %
G1 + 500 eq 4-F-phenol	86.0 %
G1 + 500 eq 4-Me-phenol (cresol)	91.1 %

These results show that the addition of 500 equivalents of *p*-cresol (**2**) afforded very similar yields compared to those obtained with phenol. 4-Methoxyphenol (**1**) gave slightly lower conversions than phenol and *p*-cresol, Electron-withdrawing groups and electronegative substituents present on the phenol moiety (**3-6**) gave lower conversions compared with those results obtained with phenol, but still better than the control without phenol.

A range of other additives were also tested, including the highly hindered BHT, naphthols, hydroquinone and catechol. Results are shown in Table 4.

Table 4: Metathesis of 1-octene with other phenols.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 500 eq hydroquinone	55.3 %
G1 + 500 eq 2-napthol	64.5 %
G1 + 500 eq catechol	75.6 %
G1 + 500 eq 4-1-napthol	76.5 %
G1 + 500 eq BHT	79.3 %
G1 + 500 eq phenol	82.0 %

The results show that the conversion of 1-octene to tetradecene is increased by the addition of BHT, napthols, hydroquinone and catechol relative to the control G1 metathesis where no phenol was added.

Example 4 - Tolerance to feed impurities

1-Alkenes derived from Fisher-Tropsch product streams may contain various impurities that are capable of retarding or even deactivating olefin metathesis catalysts. In an effort to discover whether phenolic compounds could be used in metathesis reactions of such alkene feedstocks (for example to improve catalyst lifetime, catalyst robustness and tolerance to feed impurities) the following experimental work was performed.

a) Hexanone as feed impurity

2-Hexanone was chosen as an initial model poison (impurity) because previous studies have shown that it gives rise to significant amounts of isomerized 2-alkenes during cross-metathesis reactions (for example, metathesis of 1-octene at Ru:100 ppm (G1), 50 °C with 100 eq 2-hexanone provides 15% 7-tetradecene, 7.9% *trans*-octene and 1.2 % *cis*-octene after 6 hours). Thus, G1 (100 ppm) was added to a solution of 2-hexanone (100 eq) and phenol (500 eq) in octene at 50 °C and following the general experimental procedure. The results are summarized in Table 5.

Table 5: Metathesis of 1-octene with 100 eq of 2-hexanone and 500 eq of phenol.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 100 eq 2-hexanone	8.5 %
G1 + 500 eq phenol + 100 eq 2-hexanone	87.0 %
G1 + 500 eq phenol	82.0 %

Under these conditions the conversion of 1-octene to tetradecene was almost identical to the control experiment, where no 2-hexanone is added. Most significantly, no detectable quantities of *cis*- or *trans*- 2-octene were observed during the reaction.

b) Fischer-Tropsch phenolic feed simulation

Efforts were made to test the G1 and phenol combination against a crudely simulated Fisher-Tropsch feed. An impure feed was prepared to include a range of impurities. The following compounds were added to purified Aldrich 1-octene;

Acetone (100 eq/eq Ru catalyst)

Ethanol (125 eq/eq Ru catalyst)

Toluene (70 eq/eq Ru catalyst)

Cycloheptatriene (70 eq/eq Ru catalyst)

Cyclooctadiene (60 eq/eq Ru catalyst)

1-Hexanol (60 eq/eq Ru catalyst)

2-Hexanone (60 eq/eq Ru catalyst)

Hexanal (60 eq/eq Ru catalyst)

3-Hexyne (70 eq/eq Ru catalyst)

Phenol (500 eq) was then added, followed by G1 (Ru:100 ppm) and the general experimental procedure was followed to compare 1-octene conversion against the control experiment in which no phenol was added to the impure feed. The results are shown in Table 6. These results show that upon addition G1 to 500 equivalents of phenol in the impure 1-octene feed, a greater conversion is observed compared with the control experiment in which no phenol is added

(32.8% conversion vs 6.1% conversion after 3 hours).

Table 6: 1-Octene conversion (impure feed) with 500 eq of phenol.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	6.1 %
G1 + 500 eq phenol	32.8 %

c) Untreated 1-octene

As stated under the general experimental procedure 1-octene (in this case commercial Aldrich 1-octene) is typically passed down an alumina column and stored over a bed of alumina before use. The results summarized in Table 7 below show that 1-octene cross-metathesis is possible using untreated 1-octene, giving 50% conversion after 3 hours. This result compares favourably to the control experiment, using unpurified 1-octene with no phenol, which gave rise to only 8.5 % conversion to desired product after 3 hours.

Table 7: Metathesis of 1-octene (untreated feed) with 500 eq of Phenol.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	8.5 %
G1 + 500 eq phenol	50.0 %

Example 5 - Effect of phenol on metathesis of olefins derived from Fischer-Tropsch product streams.

The general experimental procedure was used as described above.

a) FT derived Feed A

A Fischer-Tropsch (FT) derived C_7 feed with the following composition was employed:

Linear 1-alkene	86%
Linear internal alkene	1-1.5%
Branched alkene (incl. internal)	5-7%
Cyclic alkene	1-2%
Diene	1%
Oxygenate	<100ppm
Paraffins, aromatics & other	5-7%

Reactions were carried out at 50°C and at 100ppm Ru. 500 Equivalents of phenol was added relative to Ru. Conversions of 1-heptene to the desired product (6-dodecene) are shown in Table 8 below. In the control no phenol was added. It is clear that the addition of phenol improved product yields significantly despite the presence of trace poisons.

Table 8: Effect of phenol addition on Fischer-Tropsch derived C7 washed feed

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	32 %
G1 + 500 eq phenol	60 %

b) FT derived Feed B

A Fischer-Tropsch derived C_7 feed of the following composition was employed:

Linear 1-alkene	83%
Linear internal alkene	1-2%
Branched alkene (incl. internal)	4-5%
Cyclic alkene	1-2%
Diene	1-3%
Oxygenate	4-5%
Paraffins, aromatics & other	4-6%

Reactions were carried out at 50°C and at 100ppm Ru. An increasing phenol concentration was also investigated. The equivalents of phenol added were calculated relative to Ru. Results are shown in Table 9 below. It is evident that addition of phenol does improve reaction yields, and that addition of excess phenol up to a certain level (~1000 eq) further improves catalyst performance.

Table 9: The effect of phenol as additive on unwashed feed derived from a Fischer-Tropsch process.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	7 %
G1 + 500 eq phenol	12 %
G1 + 1000 eq phenol	23 %

Example 6 - Effect of phenol on ethenolysis

EXPERIMENTAL PROCEDURE:

Reactions were carried out in a 50ml Parr autoclave fitted with a stirrer, a diptube for gas entrainment, and an outlet (vent) line. The reactor was flushed with argon, sealed and flushed with ethylene. 2-Octene feed was transferred *via* syringe to an ethylene flushed sample bomb and introduced to the reactor under a few bar of ethylene pressure. The ethylene is extremely soluble in the 2-octene mixtures, thus the mixture was stirred under ethylene pressure until no further pressure drop was noted. The catalyst was weighed into a sample tube, dissolved in the solvent of interest, transferred *via* syringe to the sample bomb, and introduced to the reactor under ethylene pressure so as to reach the desired reaction pressure in the autoclave. As ethylene dissolved in the mixture and reactor pressure dropped, the pressure was maintained by opening the gas inlet line. Once the desired pressure could be maintained with no further pressure drop, the system was closed and left to stir for 15h. Samples were taken at the

end of the run and analysed by GC-FID.

Experiments were carried out at 25°C and 100ppm Ru using G1. The substrates employed were:

1) 98% 2-octene, containing 80% *cis* and 20% *trans* 2-octene.

2) 98% 2-octene, containing 99% *trans*-2-octene

Results are summarised in Table 10:

Table 10: Ethenolysis of 2-octene to 1-heptene using G1

	YIELD OF 1-HEPTENE	SELECTIVITY
2-OCTENE (4:1 CIS:TRANS)	74.5%	94.7%
2-OCTENE (4:1 CIS:TRANS) + PhOH	81.4%	92.6%
2-OCTENE (99% TRANS)	66.4%	91.5%
2-OCTENE (99% TRANS) + PhOH	79.0%	93.7%

It is evident that significantly higher yields of the desired α-olefin product were obtained with addition of phenol. When considering selectivities, these were approximately similar with and without phenol: However, phenol addition gave less isomerisation of the 1-alkene product as a side reaction but slightly more formation of 6-dodecene, the product of self-metathesis of 2-octene. While isomerisation is essentially non-reversible and leads to lower yields of desired product, equilibrium conditions mean that the longer chain byproduct can be

recycled to the reactor where it can undergo ethenolysis to generate the desired 1-alkene product. The use of phenol would, therefore, be preferred.

Example 7 - Effect of phenol where catalyst is prepared in situ.

The preparation of a Grubbs-type catalyst in a metathesis reaction medium is known. This catalyst system was reported by Nubel and Hunt in J. Molec. Catal. A, 1999, 145, 323-327 and US 6159890 and involves in situ generation of the active catalyst by the addition of $RuCl_3$, a phosphine and 1,4-butynediol diacetate (BDD) to the alkene substrate in the presence of a hydrogen sparge.

EXPERIMENTAL PROCEDURE:

Reactions were carried out in a 100 ml three-necked flask fitted with a reflux condenser, thermometer and septum. The reflux condenser was connected to a cooling bath set at 5°C to ensure a constant flow of chilled water through the jacket, thereby preventing loss of octene. The top of the condenser was connected to a bubbler in order to monitor liquid losses and gas emissions. The thermometer was positioned below the level of the reaction solution to ensure correct temperature monitoring. A needle inserted through the septum and connected to a gas supply *via* a needle valve was used to ensure a slow and steady stream of argon or hydrogen bubbles through the reaction solution. Argon was used during the initial phase to purge the system. After all the reagents

were added, the gas flow was changed to hydrogen and the reaction was heated at the desired temperature by means of a preheated oil bath, and stirred by means of a magnetic stirrer bar. Samples were taken at regular intervals *via* syringe through the septum and analysed by GC-FID. Unless otherwise stated, 20ml of octene was employed in all experiments, and catalyst, solvent and additive amounts were calculated relative to this. 0.5ml of octadecane was used as internal standard. Results are reported as the molar % yield of tetradecene.

The effect of phenol additions was tested for two different phosphine ligands namely P(cyclohexyl)$_3$ [PCy_3] and eicosyl phoban (EP) using 100ppm Ru and 500 molar eq phenol relative to Ru. It is evident from Table 11 below that the phenol effect significantly enhances the performance of this *in situ* system. In addition it is clear that this enhancement is also observed when employing alternative phosphine ligands to the standard tricyclohexylphosphine ligand.

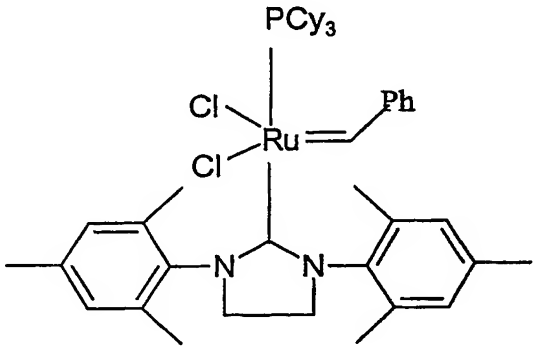
Table 11: *In situ* system: PCy_3 and EP with and without phenol at 100ppm Ru

Conditions	% Conversion of 1-Octene After 3h
100 ppm Ru, 80 degrees Ru:phenol:PCy_3:BDD = 1:0:2.5:10	30 %
100 ppm Ru, 80 degrees Ru:phenol:PCy_3:BDD = 1:500:2.5:10	67 %
100 ppm Ru, 80 degrees Ru:phenol:EP:BDD = 1: 0:2.5:10	22 %
100 ppm Ru, 80 degrees	45 %

Ru:phenol:EP:BDD = 1: 500:2.5:10	

Comparative Example 8 - Effect of phenol with a Grubbs 2nd generation catalyst (G2)

The Grubbs 2nd generation catalyst (G2) used in the present example was the compound:



This catalyst (G2) affords rapid cross-metathesis of 1-alkenes compared to G1. The comparative catalyst performance of G2 (with and without phenol) to G1 and phenol (500 equivalents per metal) was investigated for the metathesis of 1-octene following the general experimental procedure. The results are summarised in Table 12.

These results show that after 3 hours conversion afforded by the G2 catalyst in the presence of phenol is significantly lower than that afforded by G2 alone. It also clearly shows that the conversion using G1 plus phenol is similar to that using G2 alone. Additionally noticeable amounts of 2-octene and secondary

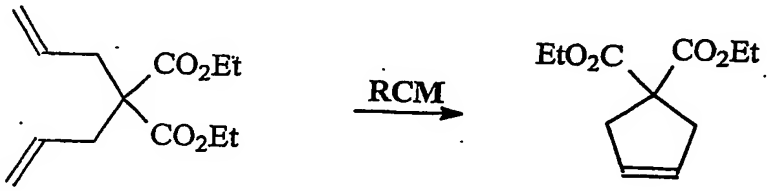
metathesis products (SMP) were observed when G2 was employed in the absence of phenol. These SMP compounds are not observed when using G1 with added phenol.

Table 12: Conversion of 1-octene with G2, (without phenol), G1 + 500eq phenol and G2 + 500eq phenol.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G2 with no phenol added	91.2 %
G2 + 500 eq phenol	68.9 %
G1 + 500 eq phenol	82.0 %

Comparative Example 9 - Effect of phenol on ring closing metathesis

In this investigation diethyl diallyl malonate was used as a starting material and was converted to the ring-closed product using G1.



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G1 catalyst was weighed into a custom-made miniature aluminium weighing tray. An amount of 11.2 mg of the catalyst provided a Ru concentration of 100ppm.

The weighing tray containing the catalyst was added to a solution of diethyl diallyl malonate (13.5 ml, 4000 eq) dissolved in 15 ml CH_2Cl_2 at 50 °C, and the reaction stirred for 6 hours. GC samples were taken thereafter every 10, 30, 60, 120, 180, 240 and 360 minutes.

An identical reaction was set-up in which 500 equivalents of phenol was added to a solution of diethyl diallyl malonate (13.5 ml, 4000 eq) dissolved in 15 ml CH_2Cl_2 at 50 degrees before G1 was added. The results are summarized in Table 13. These results show that the addition of phenol *retards* RCM of diethyl diallyl malonate.

Table 13: Ring-Closing Metathesis of diethyl diallyl malonate using G1 and G1 + 500 eq phenol.

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	39.0 %
G1 + 500 eq phenol	25.4 %

Comparative Example 10

Non-phenolic additives that are structurally related to phenol were used in a metathesis reaction set out in the general experimental procedure. That is the phenol additive was in each case replaced with a non-phenolic additive using 500 molar equivalents of additive to Ruthenium catalyst.

The results indicate that these additives do not exhibit the beneficial effect in metathesis observed for the phenolic compounds reported above.

Table 14: Metathesis of 1-octene with non-phenolic additives

Conditions	% Conversion of 1-Octene After 3h
G1 with no phenol added	26.5 %
G1 + 500 eq aniline	0 %
G1 + 500 eq thiophenol	0 %
G1 + 500 eq cyclohexanol	13.4 %
G1 + 500 eq anisole	17.8 %
G1 + 500 eq phenol	82.0 %

It will be appreciated that many variations in detail are possible without thereby departing from the scope of the invention.

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